

Synthesis and Characterization of Polyaniline Based Conducting Polymers

M. B. Wasu¹ and A. R. Raut²

¹Research Student,
Government Vidarbha Institute of Science and Humanities,
Amaravati, M. S., INDIA.

²Reader,
Government Vidarbha Institute of Science and Humanities,
Amaravati, M. S., INDIA.

(Received on: April 4, 2014)

ABSTRACT

Present work deals with the synthesis of Polyaniline, polynitro aniline, poly m-toludine and poly o-toludine polymers by chemical oxidation method using ammonium per sulfate as chemical oxidant. The yield of all polymers was higher than 90%. The synthesized polymeric material have been characterized by FTIR spectroscopy. FTIR and SEM studies of polymer show the structural and slight morphological changes with change in substituent in monomer units.

Keywords: Polyaniline, polynitro aniline, poly m-toludine, poly o-toludine, ammonium per sulfate.

INTRODUCTION

The conducting polymers were emerged as materials of current research worldwide. The conducting polymers have mechanical parameters of polymers as well as electrical properties of semiconductors. Among the various conducting polymers polyaniline and its derivatives are intensively studied, because of their good

environmental, chemical, thermal stability.¹⁻⁶ These conducting polymers can be synthesized chemically or electrochemically^{7,8}. The special characteristics of polyaniline is that it can be doped or undoped by reacting with acidic or alkaline environment without any change in number of π electrons.⁹ This can be possible because of presence of NH and N groups in polymer backbone. These groups on protonation or

deprotonation bring the changes in color and electronic conductivity¹⁰. The amine or imine nitrogen atom in any compound can be protonated by protonic acids.¹¹ This doping and undoping property gives the Pani and its analogous polymers enormous industrial applications¹². Protonation or doping of polyaniline by acids can be done during polymerization of aniline in presence of acids in polymerization solution¹³ or after polymerization by adding polymer in acid solution¹⁴. Type of acid and concentration of acid affect the degree of polymerization of of amine and imine sites in polymer¹⁵. Different forms of form has conductivity on semiconductor level (of the order of 10^0Scm^{-1}), much more higher than common polymers ($<10^{-9} \text{Scm}^{-1}$) but lower than typical metals ($>10^4 \text{Scm}^{-1}$). Pani hydrochloride i.e. protonated pani convert to non conducting blue emeraldine polyaniline have different physical and chemical properties.^{16,17} The green protonated emeraldine base when treated with ammonium hydroxide.¹⁸⁻²⁰ Pani and pani based other conjugated polymers have presence of unique π electrons, the wave function of these electrons are delocalized over a long portion of polymer chain when molecular structure of the backbone is planar.

EXPERIMENTAL

1.1 Synthesis of polyaniline

Aniline (Merck) was used after distillation. Ammonium per sulfate, hydrochloric acid is of analytical grade. 25 ml freshly distilled aniline was added to 500 ml 2M Hydrochloric acid 250 ml of 0.25 M APS $(\text{NH}_4)_2\text{S}_2\text{O}_8$ solution was added from a burette into well stirred monomer solution

within 40 min. The polymerization was carried out at room temp. The solution was continuously stirred for 24 hours after addition of oxidant. The green dark powder obtained was washed with dil HCl, distilled water and methanol. The synthesized powder was treated with ammonia solution (0.5) for four hour at room temp in order to convert the polymer into emeraldine base (EB).

1.2 Synthesis of poly m-toludine

10 ml m-toludine was mixed with 500ml 1M HCl, stirred for six hours 22g Ammonium peroxy disulfate was dissolved in 200ml 1M HCl. APS solution was gradually mixed in meta toludine monomer solution, blakish violet color was developed. Stirring was continued for 24 hour with magnetic stirrer. The blue ppt. obtained was washed with distilled water and methanol. The product obtained was dissolved in 0.5M ammonia solution. The greenish blue colored product was dried in oven at 60°C for 12 hours.

1.3 Synthesis of poly o-toludine

10 ml o-toludine was mixed with 500 ml 1M HCl. APS solution was gradually mixed in, monomer solution. The reaction mixture was stirred for 24 hours and then filtered. The greenish violet ppt was washed with distilled water and methanol and was dissolved in 0.5 M ammonia solution for four hour. The filtered product was dried in oven at 60°C for 12 hours.

1.4 Synthesis of polynitro aniline

Nitrating mixture was prepared by mixing 10 ml H_2SO_4 and 4ml nitric acid,

mixture was cooled. To this nitrating mixture, 3 g polyaniline was added, the mixture was refluxed using air condenser at 40 °C for 2 hours. The product solution was cooled and poured in 100 ml distilled water, stirred and filtered. Product obtained was washed with water methanol and the product was dissolved in ammonia solution. The filtered product was dried in oven at 60 °C for 5 hour.

RESULTS AND DISCUSSION

FTIR spectra were obtained using Spectrophotometer of Bruker make, Germany Model (3000Hyperion Microscope with vertex 80 FTIR System). Morphology of synthesized polymers were studied by Field Emission Gun Scanning Electron microscopes (FEG SEM). Model-JSM-7600F, Resolution 1.0nm (15kv.)

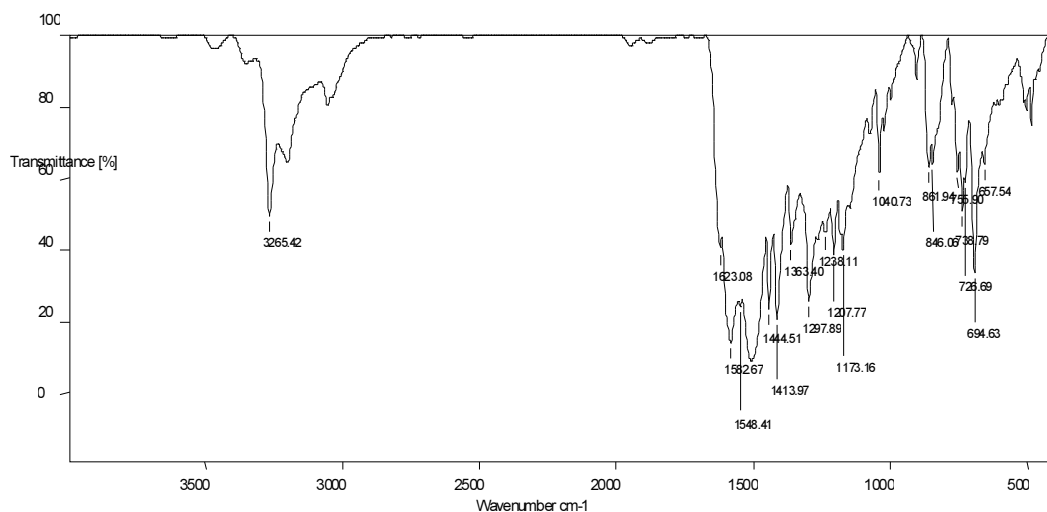


Fig.1

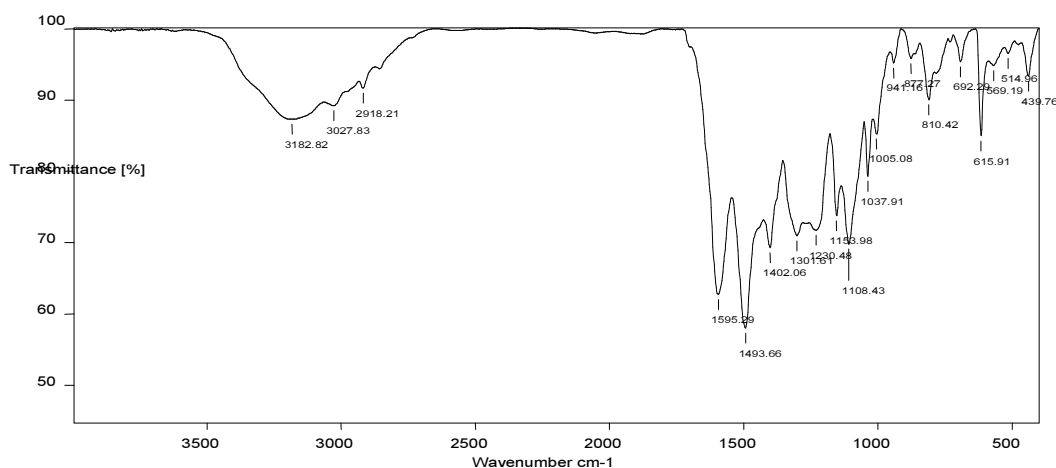
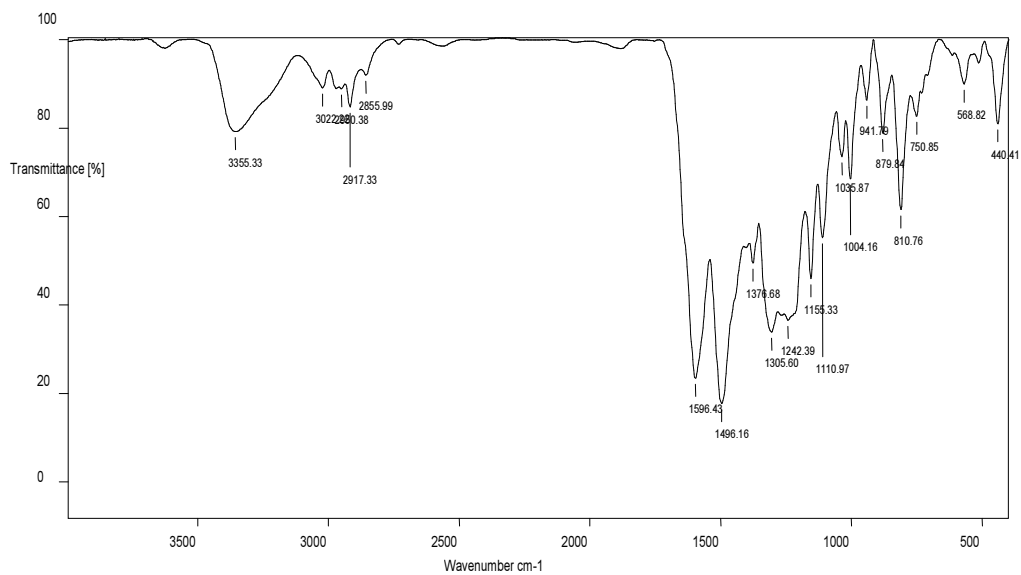
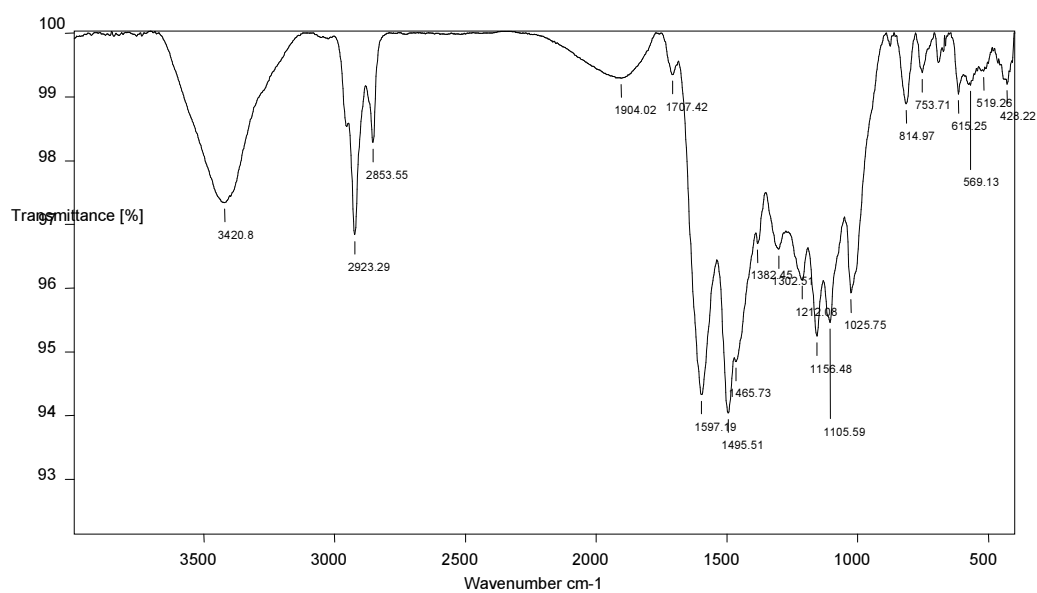


Fig.2

**Fig.3****Fig.4**

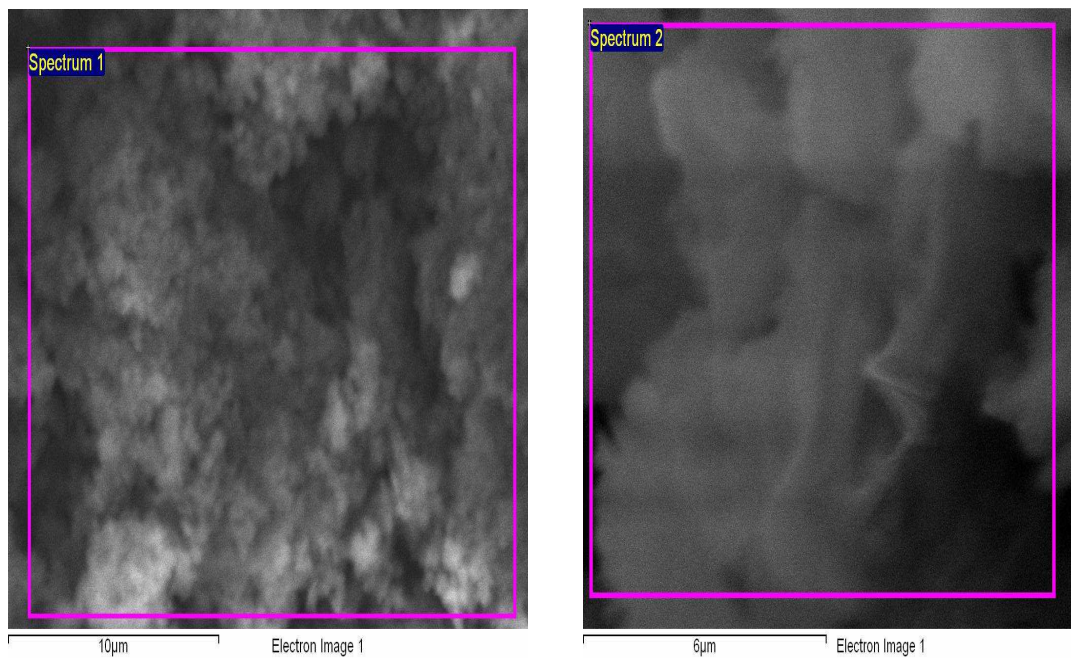


Fig.5,6

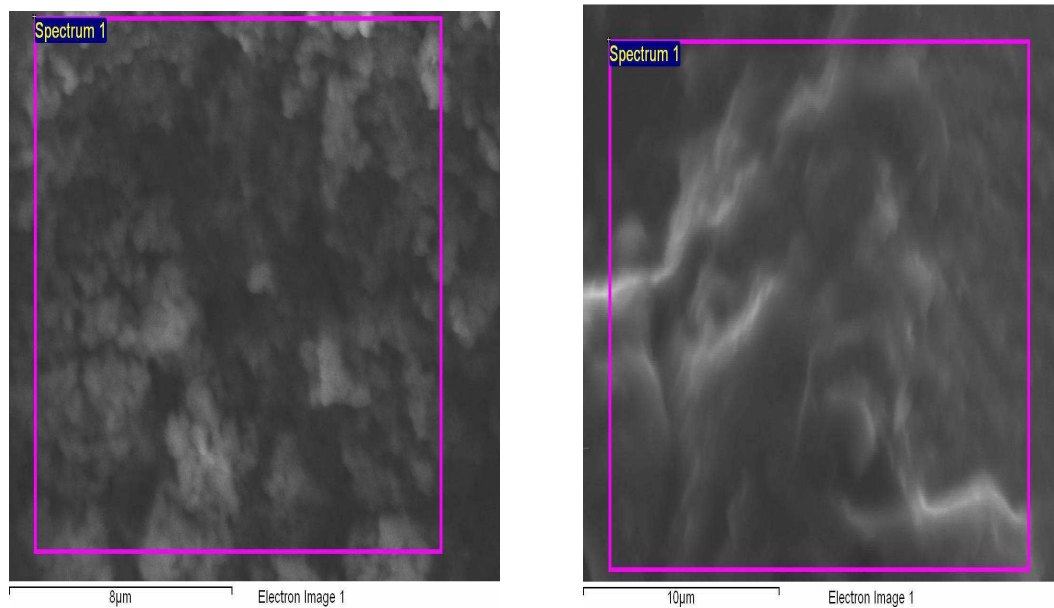


Fig.7,8

quinoid-benzenoid-quinoid ring. C-H stretching vibrations in benzenoid ring vibration mode. Peak at 1110 cm^{-1} is assigned to methyl substituted benzenoid and quinoid ring. $940, 879, 750\text{ cm}^{-1}$ corresponds to C.

Fig.1 shows FTIR spectra of polyaniline. As is shown from the fig. 3265 cm^{-1} corresponds to then N-H stretching mode of secondary amine. $1600-1450\text{ cm}^{-1}$ this region is assigned for for N-H deformation, Aromatic ring breathing, C=N stretching. 1,4 substituted benzene ring may give absorption at $1600-1580\text{ cm}^{-1}$. The peaks at 1582 cm^{-1} and 1548 cm^{-1} is assigned to the benzenoid and quinoid form of PANI backbone.^{19,20} $1400-1200\text{ cm}^{-1}$ is C-N stretching region for aromatic amines. $1200-500\text{ cm}^{-1}$ is the region for in plane and out of plane bending of C-H in aromatic ring. Peak at 1302 cm^{-1} is assigned to C-N oscillations in benzene ring. The peak at 1173 cm^{-1} corresponds to C-H in plane oscillations.

Fig. 2 shows the FTIR spectra of m-toluidine. The broad band observed in spectra at 3182 cm^{-1} is assigned to N-H stretching mode. The characteristic band at 2918 cm^{-1} show Vibrations of $-\text{CH}_3$ group. The peak at 1595 cm^{-1} and 1493 cm^{-1} are assigned to the stretching vibrations of benzenoid and quinoid ring. The peak appearing at 1402 cm^{-1} indicates the symmetric deformation of $-\text{CH}_3$ group. 1301 cm^{-1} and 1230 cm^{-1} corresponds to the C-N vibration. The peak at 1153 cm^{-1} is assigned to C-H stretching of benzenoid ring. The 1108 cm^{-1} peak is assigned to C-C stretching vibrations of methyl substituted benzenoid and quinoid structure. The prominent peaks at

$941, 877, 810\text{ cm}^{-1}$ assigned to an out of plane C-H vibrations and 1,2,4 substituted benzenoid ring and in plane C-H vibrations quinoid ring. The peak at 692 cm^{-1} . C-H bending and 615 cm^{-1} indicate aromatic ring deformation. The peaks at $569, 514$ and 439 cm^{-1} corresponds C-C stretching in benzenoid ring, C-C stretching and C-N stretching in benzenoid and quinoid structures respectively.

Fig.3 shows the FTIR spectra of poly o-toluidine. 3355 cm^{-1} is assigned to N-H stretching. Peak at $2917, 2855\text{ cm}^{-1}$ corresponds to the C-H stretching due to substituted methyl group. 1596 cm^{-1} peak indicate C-N stretching of quinoid structure. 1376 cm^{-1} peak is assigned to C=N⁺ stretching vibrations¹⁸. 1305 and 1242 cm^{-1} peaks corresponds to C-N vibrations in alternate units of H out of plane vibrations. C-C stretching vibrations of benzenoid ring are indicated by peak at 568 cm^{-1} ²¹. 440 cm^{-1} peak is assigned to C-N stretching in benzenoid and quinoid ring.

Fig.4 shows the FTIR spectra of Polynitro aniline. Peak at 3420 cm^{-1} indicate N-H stretching. The characteristic peaks at $1597, 1495\text{ cm}^{-1}$ corresponds to asymmetric and symmetric stretching vibrations in NO_2 group. The absorption band at 1302 cm^{-1} indicate C-N vibrations in alternate units of semiquinoid and quinoid ring. $1212-428\text{ cm}^{-1}$ is the region of in plane and out of plane C-H bending in aromatic ring. 753 cm^{-1} corresponds to in plane bending of C- NO_2 . 615 cm^{-1} peak is assigned to aromatic ring deformation.

Fig.5,6,7,8 shows the SEM images of Polyaniline, poly m-toluidine, poly o-toluidine, poly nitroaniline respectively.

Characterization of synthesized polymers was also carried out using scanning electron microscopy (SEM). All electron micrographs were obtained from the powdered form of polymers. SEM micrograph of polymers in base form gives a smooth and homogeneous appearance. SEM images shows the differences in morphologies of the polymers.

CONCLUSION

PANI based polymers have been successfully synthesized by using chemical oxidation method. SEM images shows the amorphous nature of polymers. FTIR spectra obtained in the work are in agreement with FTIR characterization reported in the literature and comparison with standards²³. So FTIR spectra confirm the formation of Polyaniline, Poly m-toluidine, Poly o-toluidine, polynitroaniline. Results shows that Poly o-toluidine and Poly m-toluidine N-H stretching bands become more broad indicating the extensive h-bonding between the polymeric strands. SEM studies shows that smooth and homogeneous morphology with slight differences due to nature and position of group in monomer. Further studies in progress is focused on the doping of lanthanide metals in these synthesized polymers and effect of doping on their conductivity.

Acknowledgement- Authors are thankful to the Chemical analysis lab, SAIF, IIT, Bombay for extending FTIR and SEM facilities.

REFERENCES

1. Z. Hau, J Shi L.Zhang, M. Rcan. *Adv. Matter*, 14,830 (2002).
2. H. Naarman, Science and Application of conducting polymer, *Adam Hilger, Briistal*, (1991).
3. Trivedi, D.C. In Handbook of Organic conductive molecules and Polymers, Nalwa, H. S.Ed., Wiley, *Chinchester, England*, Vol 2, p 505 (1993).
4. Pranon Jyoti Saikia, Pratap Chandra Samarth, *Material Science and Applications*, 2,1022-1026 (2011).
5. Dasquali M, Pistoia G. Rosati R., *Synthetic Metals*, 53, 1-15 (1990).
6. Stejaslal, J. and R. G. Gilbert, Polyaniline preparation of a conducting polymer (IUPAC Technical report), *Pure Appl. Chem.*, 74,857-867 (2002).
7. M. Bammahd Keivani, K. Zare, M. Aghaie , H. Aghaie, M. Monajjemi, *E journal of Chemistry*, 7(1), 105-110 (2010).
8. Angelopoulos M, Ravnd A, Macdiarmid A G and Epstein A., *Synthetic Metals*, 21,21-30 (1987).
9. Chen S.A., Lin L.C. polyaniline doped by new class of dopants, ionic salts, structure and properties, *Macromolecules*, 28, 1239-1245 (1995).
10. Kous S. Chandra R Dhawan S.K., Sons Actuators B, *Chem*, 75,151-159 (2000).
11. MacDiarmid A.G. Epstein A.J., *Farad, Discuss, Chem. Soc.*, 88,317-332 (1989).
12. Abdolreza, Mirmohseni, Ali Ola degaragoze, Farshad Fotoohifar, *Iranian Polymer Journal*, 16(1),3-12 (2007).
13. Leyva M.E. Barra G.M.O., Soares B.G., *Synth Net.*, 123,443-449 (2001).
14. Luthr V., Singh R., Gupta S.K., Mansingh A., *Curr. Appl. Phys*, 3,219-222 (2003).
15. Laska J, *Synth Met.*, 129,229-233 (2002).
16. B.G.Levi, *Phys Today*, 2000, 53(12),19.

17. A. G. MacDiarmid, *Angew, Chem. Int.Ed.*, 40, 2581 (2001).
18. Bhadani S N Gupta M K and SK S. J. *Appl Polym Sci*, 49, 397-403 (1993).
19. J.Stejskal P.Kartochvil, A.D. Jonkins, *Polymer*, 37, 367 (1996).
20. Biswa Rajan Sarangi, Matru Prasad Dash, *Int. Journal of Adv Research*, Vol. 1, Issue 4, 217-222 (2013).
21. Organic Spectroscopy by Willam kemp.
22. Savitha P, Sathyanarayana D.N. *J Polym Sci; Part A, Poly Chem*, 42,6109 (2004).
23. N.Chandrakanthmal and M.A. Careem, *Polymer Bulletin*, 44, 101-108 (2000).